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Abstract

Full Text

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SYNTHESIS AND PROPERTIES OF PHENYL-, 3,4-XYLYL-, AND 4-ISOPROPYLPHENYLALKYLSILANES

In recent years much attention has been devoted to the synthesis and study of the physicochemical and technical properties of silicon hydrocarbons of various structures. Of great interest are silicon hydrocarbons containing aryl and alkyl radicals bonded to a silicon atom—arylalkylsilanes.

In a previous communication ⁽¹⁾ we described mono-, di-, and tri-*n*-tolylalkylsilanes. The present work describes the preparation and properties of phenylalkylsilanes, 3,4-xylylalkylsilanes, and 4-isopropylphenylalkylsilanes.

Of the 3,4-xylylalkylsilanes only one, 3,4-xylyltrimethylsilane, is known ⁽²⁾. 4-Isopropylphenylalkylsilanes have not been described in the literature.

We synthesized phenylalkylsilanes in order to compare their physicochemical properties with those of other arylalkylsilanes. A number of phenylalkylsilanes were obtained by us for the first time.

All the phenylalkylsilanes obtained were prepared with the aid of magnesium- and lithium-organic compounds.

3,4-Xylylalkylsilanes (Table 1) were obtained by the interaction of 3,4-xylyllithium with the corresponding alkylhalo(ethoxy)silanes. 3,4-Xylyllithium was obtained from 4-bromo-*o*-xylene, prepared by bromination of *o*-xylene. 4-Bromoisopropylbenzene was obtained analogously; on its basis, via lithium-organic compounds, di-4-isopropylphenyldimethylsilane and di-4-isopropylphenyldiethylsilane were obtained.

The physicochemical properties of phenyl-, 3,4-xylyl-, and 4-isopropylphenylalkylsilanes are presented in Table 1.

Phenyltrimethylsilane. To phenylmagnesium bromide, prepared from 48 g of magnesium and 318 g of bromobenzene, 108 g of trimethylchlorosilane was added. The mixture was heated for 18 h. Obtained: 62 g (yield 41.3%).

Phenyltriethylsilane. To ethylmagnesium bromide, prepared from 72 g of magnesium and 328 g of ethyl bromide, 105 g of phenyltrichlorosilane was added. The mixture was heated for 15 h. Obtained: 78 g (yield 81.5%).

Phenyltripropylsilane. To propylmagnesium bromide, prepared from 72 g of magnesium and 366 g of propyl bromide, 105 g of phenyltrichlorosilane was added. The mixture was heated for 15 h. Obtained: 80 g (yield 68.5%).

Phenyltributylsilane. To butylmagnesium bromide, prepared from 72 g of magnesium and 411 g of butyl bromide, 105 g of phenyltrichlorosilane was added. The mixture was heated for 15 h. Obtained: 70 g (yield 50.7%).

Diphenyldimethylsilane. To phenylmagnesium bromide, prepared from 24 g of magnesium and 157 g of bromobenzene, 64.5 g of dimethyldichlorosilane was added. The mixture was heated for 12 h. Obtained: 83.5 g (yield 78.9%).

Diphenyldiethylsilane. To phenylmagnesium bromide, prepared from 84 g of magnesium and 471 g of bromobenzene, 127 g of diethyl-

Table 1

Compound	Formula	Hg	b.p., °C/mm	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
Phenyl- ⁽³⁾	$C_6H_5Si(C_3H_7)_3$	100	125/0	0.8722	1.4908	49,88	49,95	—	—	—	—
Phenyl- ⁽⁴⁾	$C_6H_5Si(C_4H_9)_3$	100	132/0	0.8915	1.5003	63,48	63,84	—	—	—	—
Phenyl- ⁽⁵⁾	$C_6H_5Si(C_3H_7)_2(C_2H_5)$	100	129/9	0.8799	1.4950	77,01	77,73	76,82	7,73	73,22	11,18
Phenyl- ⁽⁶⁾	$C_6H_5Si(C_4H_9)_2(C_2H_5)$	100	142/4	0.8753	1.4915	91,42	91,62	78,25	7,78	70,64	11,59
Diphenyl- ^(5,6)	$(C_6H_5)_2Si(C_2H_5)_2$	100	115/4	0.8898	1.5628	69,67	69,62	—	—	—	—
Diphenyl- ⁽⁷⁾	$(C_6H_5)_2Si(C_2H_5)(C_3H_7)$	100	135/3	0.8844	1.5600	78,96	78,88	—	—	—	—
Diphenyl- ⁽⁸⁾	$(C_6H_5)_2Si(C_2H_5)(C_4H_9)$	100	144/4	0.8951	1.5476	88,31	88,22	80,77	8,09	80,99	9,01
Diphenyl- ⁽⁹⁾	$(C_6H_5)_2Si(C_2H_5)(C_3H_7)$	100	152/3	0.8923	1.5404	97,74	97,40	81,05	8,10	80,89	9,51
Diphenyl- ⁽¹⁰⁾	$(C_6H_5)_2Si(C_2H_5)(C_4H_9)$	100	182/5	0.9104	1.5338	107,24	106,66	81,81	8,17	81,12	9,34

Compound	Formula	Hg	b.p., °C/mm	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
3,4-Xylyltrimethylsilane ⁽⁸⁾	$3,4-(C_6H_4)_2Si(CH_3)_3$	175.16	75/6	1.3754	1.4983	59.89	59.21	—	—	—	—
3,4-Xylyltriethylsilane	$3,4-(C_6H_4)_2Si(C_2H_5)_3$	117/4	50/6	1.3963	1.5003	73.57	73.29	76.2776	11.1911	76.127	10.98
3,4-Xylyltripropylsilane	$3,4-(C_6H_4)_2Si(C_3H_7)_3$	147/6	50/6	1.3829	1.5027	87.76	87.02	77.3877	11.5311	77.179	11.50

Table 1 (continued)

Compound	Formula	Hg	b.p., °C/mm	d_4^{20}	n_D^{20}	MR_D , found	MR_D , calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H
3,4-Xylyltributylsilane	$3,4-(C_6H_4)_2Si(C_4H_9)_3$	156/4	75/6	1.3783	1.4989	101.66	100.88	78.9879	11.0971	78.88	11.92
Di-3,4-xylyldimethylsilane	$(3,4-(C_6H_4)_2Si(CH_3)_2)$	54.5	55.5	—	—	—	—	80.6280	9.6390	80.55	9.01
Di-3,4-xylyldiethylsilane	$(3,4-(C_6H_4)_2Si(C_2H_5)_2)$	61.2	61.3	1.3770	1.5055	98.71	97.40	80.8080	11.1695	81.01	9.51
Di-3,4-xylyldipropylsilane	$(3,4-(C_6H_4)_2Si(C_3H_7)_2)$	88/4	63/7	1.3727	1.5072	106.00	106.66	81.6381	11.0210	81.41	9.95
Di-3,4-xylyldibutylsilane	$(3,4-(C_6H_4)_2Si(C_4H_9)_2)$	41—	42	—	—	—	—	82.0482	11.2510	81.75	10.30
Di-4-isopropylphenylmethylsilane	$(4-(CH_3)_2CHC_6H_4)_2Si(CH_3)$	168/4	142	1.3770	1.5072	98.21	97.40	81.1281	11.0348	81.01	9.51
Di-4-isopropylphenylethylsilane	$(4-(CH_3)_2CHC_6H_4)_2Si(C_2H_5)$	171/6	147	1.3710	1.5072	107.64	106.66	81.5881	11.0497	81.45	9.93

dichlorosilane. The mixture was heated for 15 h. Obtained: 95 g (yield 49%).

Diphenyldipropylsilane. To phenyllithium, prepared from 6 g of lithium and 65 g of bromobenzene, 41 g of dipropyldiethoxysilane was added. The mixture was heated for 8 h. Obtained: 17.8 g (yield 35%).

Diphenyldibutylsilane. To phenyllithium, prepared from 3.5 g of lithium and 37 g of bromobenzene, 20 g of dibutyldiethoxysilane was added. The mixture was heated for 8 h. Obtained: 15.8 g (yield 54%).

Diphenyldiisoamylsilane. To phenyllithium, prepared from 2.5 g of lithium and 23.9 g of bromobenzene, 18 g of diisoamyldiethoxysilane was added. The mixture was heated for 10 h. Obtained: 9.7 g (yield 43%).

3,4-Xylyltrimethylsilane. To 3,4-xylyllithium, prepared from 6 g of lithium and 76 g of 4-bromo-*o*-xylene, 43.2 g of trimethylchlorosilane was added. The mixture was heated for 8 h. Obtained: 41.5 g (yield 57.7%).

3,4-Xylyltriethylsilane. To 3,4-xylyllithium, prepared from 2.5 g of lithium and 33 g of 4-bromo-*o*-xylene, 40 g of triethylbromosilane was added. The mixture was heated for 8 h. Obtained: 21 g (yield 46%).

3,4-Xylyltripropylsilane. To 3,4-xylyllithium, prepared from 2.8 g of lithium and 37 g of 4-bromo-*o*-xylene, 42.8 g of tripropyldiethoxysilane was added. The mixture was heated for 8 h. Obtained: 30 g (yield 57%).

3,4-Xylyltributylsilane. To 3,4-xylyllithium, prepared from 2.5 g of lithium and 30 g of 4-bromo-*o*-xylene, 36.2 g of tributylethoxysilane was added. The mixture was heated for 8 h. Obtained: 15.5 g (yield 33%).

Di-3,4-xylyldimethylsilane. To 3,4-xylyllithium, prepared from 8.4 g of lithium and 92.5 g of 4-bromo-*o*-xylene, 28.2 g of dimethyldichlorosilane was added. The mixture was heated for 8 h. Obtained: 40.5 g (yield 69%).

Di-3,4-xylyldiethylsilane. To 3,4-xylyllithium, prepared from 6.9 g of lithium and 83 g of 4-bromo-*o*-xylene, 32 g of diethyldichlorosilane was added. The mixture was heated for 8 h. Obtained: 38.5 g (yield 68.5%).

Di-3,4-xylyldipropylsilane. To 3,4-xylyllithium, prepared from 3 g of lithium and 39 g of 4-bromo-*o*-xylene, 18 g of dipropyldichlorosilane was added. The mixture was heated for 8 h. Obtained: 16.5 g (yield 51%).

Di-3,4-xylyldibutylsilane. To 3,4-xylyllithium, prepared from 7 g of lithium and 92 g of 4-bromo-*o*-xylene, 50 g of dibutyldiethoxysilane was added. The mixture was heated for 8 h. Obtained: 33 g (yield 40%).

Di-4-isopropylphenyldimethylsilane. To 4-isopropylphenyllithium, prepared from 5.6 g of lithium and 79.6 g of 4-bromoisopropylbenzene, 26 g of dimethyldichlorosilane was added. The mixture was heated for 8 h. Obtained: 36 g (yield 61%).

Di-4-isopropylphenyldiethylsilane. To 4-isopropylphenyllithium, prepared from 7 g of lithium and 90 g of 4-bromoisopropylbenzene, 33 g of

diethyldichlorosilane was added. The mixture was heated for 8 h. Obtained: 50.7 g (yield 73.6%).

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